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US Army Research Laboratory

Theoretical Prediction of the Heats of Formation, Densities, and Relative Sensitivities for 1,7-dinitro-3,4,5,8-tetra N-oxide-bis([1,2,3]triazolo)[4,5-b:5',4'-e]pyrazine, 1,7-dinitro-3,5,8-tri N-oxide-bis([1,2,3]triazolo)[4,5-b:5',4'-e]pyrazine, 1,7-dinitro-3,5-bis N-oxide-bis([1,2,3]triazolo)[4,5-b:5',4'-e]pyrazine, 1,7-dinitro-1,7-dihydrobis([1,2,3]triazolo)[4,5-b:4',5'-e]pyrazine

by Edward FC Byrd

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Weapons and Materials Research Directorate, ARL

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14. ABSTRACT

Using the US Army Research Laboratory–developed series of scripts, written to dramatically simplify the computation of crystalline density and heat of formation, the performance properties for the 1,7-dinitro-3,4,5,8-tetra N-oxide-bis([1,2,3]triazolo)[4,5-b:5',4'-e]pyrazine (1), 1,7-dinitro-3,5,8-tri N-oxide-bis([1,2,3]triazolo)[4,5-b:5',4'-e]pyrazine (2), 1,7-dinitro-3,5-bis N-oxide-bis([1,2,3]triazolo)[4,5-b:5',4'-e]pyrazine (3), 1,7-dinitro-1,7-dihydrobis([1,2,3]triazolo)[4,5-b:4',5'-e]pyrazine (4) notional energetic materials were evaluated. Additionally, a qualitative estimation of the impact sensitivities has been calculated. This report outlines the procedures used to generate this information, as well as Cheetah calculations, using the predicted crystalline density and heat of formation.

15. SUBJECT TERMS

computational toolkit, quantum molecular dynamics, computational toolbox, script, crystalline density, heat of formation, impact sensitivity, energetic materials

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1. Introduction

US Army Research Laboratory (ARL) researchers have achieved robust theoretical models capable of predicting performance properties, such as heats of formation,[1,2] densities,[3,4] and impact sensitivity[5] of energetic materials and have begun growing advanced synthesis capabilities to realize notional materials. This dual capability allows synthetic and formulation chemists to safely and quickly screen candidate materials to focus efforts only on the most promising compounds. For an in-depth explanation of the different theoretical methods employed herein, please refer to previous works.[6,7]

This technical note will detail theoretical predictions of heat of formation, density, sensitivity and performance for the 1,7-dinitro-3,4,5,8-tetra N-oxide bis([1,2,3]triazolo)[4,5-b:5',4'-e]pyrazine (**1**), 1,7-dinitro-3,5,8-tri N-oxide-bis([1,2,3]triazolo)[4,5-b:5',4'-e]pyrazine (**2**), 1,7-dinitro-3,5-bis N-oxide-bis([1,2,3]triazolo)[4,5-b:5',4'-e]pyrazine (**3**), 1,7-dinitro-1,7-dihydrobis([1,2,3]triazolo)[4,5-b:4',5'-e]pyrazine (**4**).[8]

2. Results and Discussion

The properties of **1**, **2, 3**, **4** (Fig. 1a–d) were predicted using the ARL tools.[7] For the estimation of the impact sensitivities, the electrostatic maps on the 0.001 isosurfaces were generated with the scalar range of the electrostatic surface potential (ESP) ranging from –0.05 to 0.075. Recall that for this visualization methodology, regions of large positive charge (i.e., electron deficient regions, labeled as red) over the backbone of the structure tend to indicate increased sensitivity.

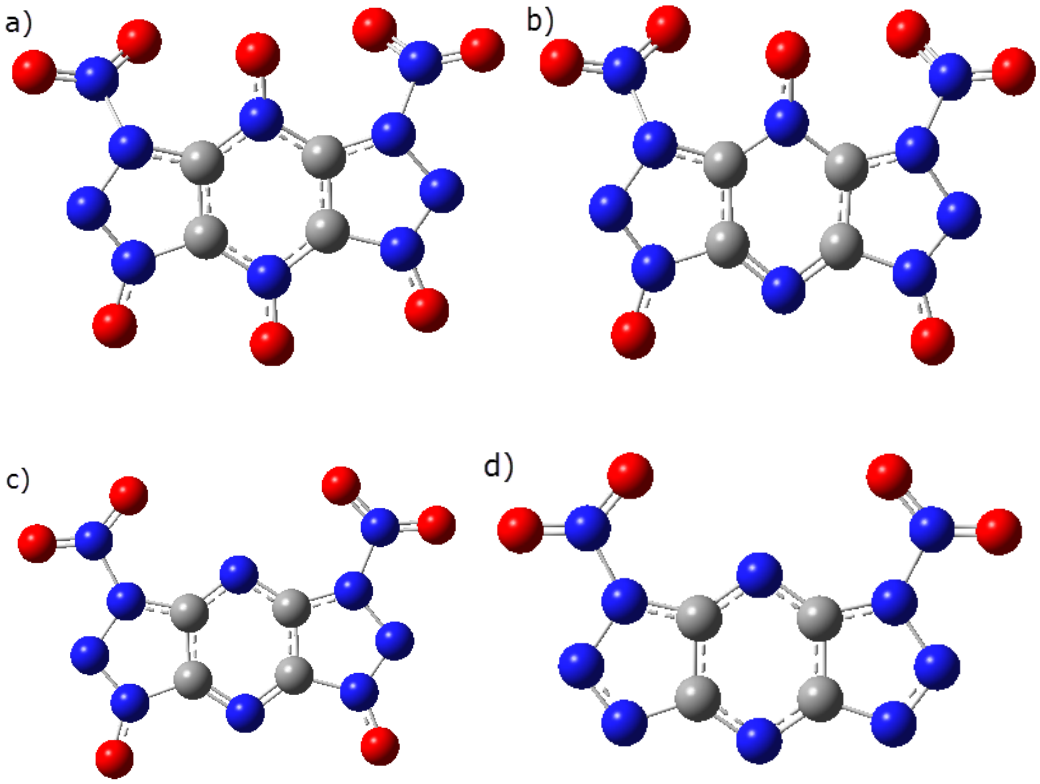

Fig. 1 Optimized structure of a) 1, b) 2, c) 3, d) 4

The computed heats of formation and crystalline densities for these molecules are presented in Table 1.

Table 1 Computed heats of formation and crystalline densities for the molecules

Molecule	Solid phase heat of formation (kcal/mol)	Density (g/cm3)
1	230.199	2.038
2	215.463	1.997
3	204.528	1.970
4	207.026	1.885

Additionally, we plot the ESP maps for **1** (Fig. 2a–b), **2** (Fig. 3a–b)**, 3** (Fig. 4a–b), and **4** (Fig. 5a–b) with and without the molecule overlaid on the ESP. When the images are analyzed, we would quantify the molecules as sensitive for all molecules, with the possible exception of molecule **4**, which could be slightly less sensitive than the others. We performed Cheetah 7.0 calculations[9] to predict the performance parameters using the predicted heats of formation and densities. At the Chapman-Jouguet point, Cheetah yields the values shown in Table 2.

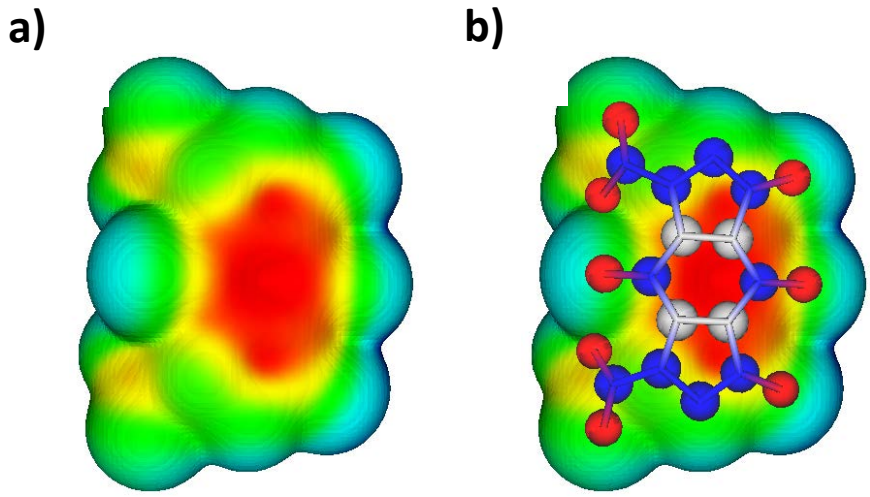

Fig. 2 Electrostatic potential map of 1, without a) and with b) molecule overlay

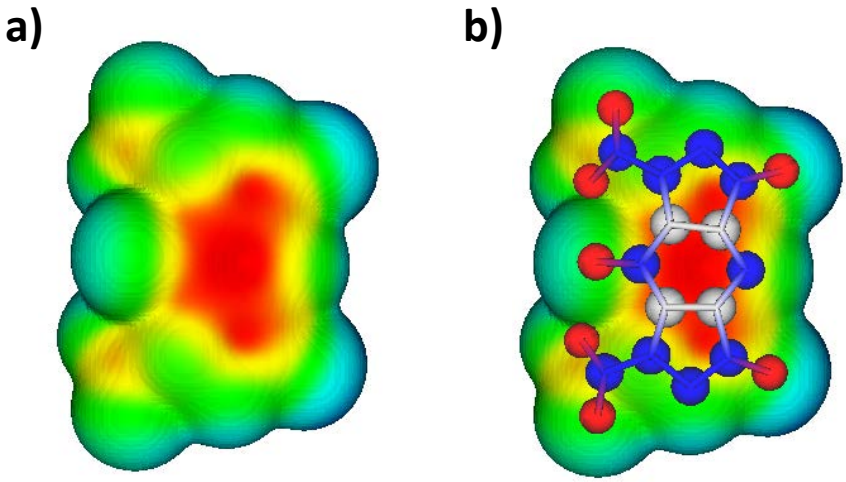

Fig. 3 Electrostatic potential map of 2, without a) and with b) molecule overlay

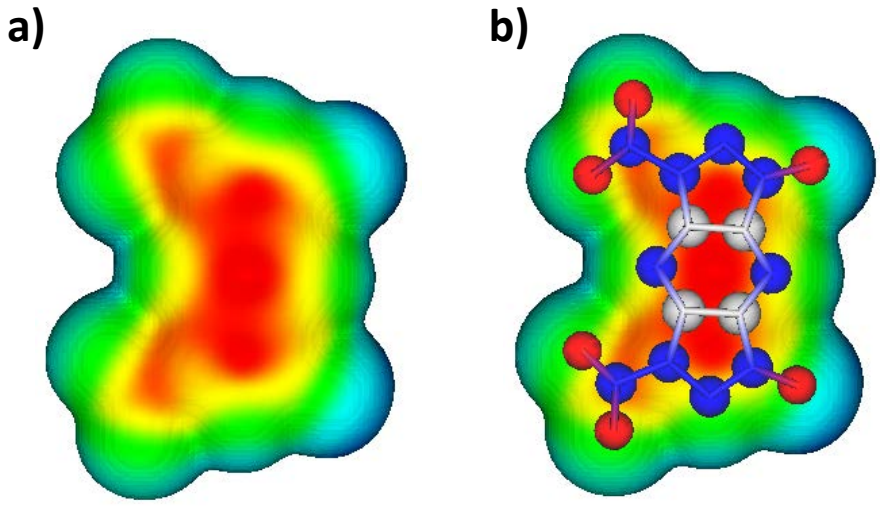

Fig. 4 Electrostatic potential map of 3, without a) and with b) molecule overlay

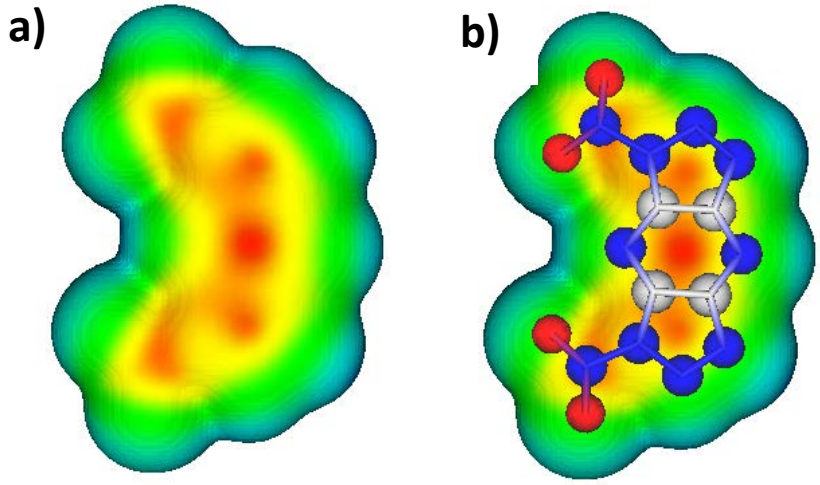

Fig. 5 Electrostatic potential map of 4, without a) and with b) molecule overlay

Table 2 Cheetah predicted properties for 1, 2, 3, and 4

Molecule	Pressure (GPa)	Shock velocity (km/s)	Temperature (K)	Total energy of detonation (TNT eqv) (per g/cm3)	Total energy of detonation (TNT eqv) (per g)
1	59.148	10.278	5288.9	2.358	1.914
2	53.617	10.118	5065.5	2.107	1.745
3	48.710	9.973	4751.5	1.870	1.570
4	38.298	9.424	4142.3	1.534	1.346

Note: TNT = trinitrotoluene

3. Conclusions

The ARL-developed software tools were used to predict the heats of formation and crystalline densities of the 1,7-dinitro-3,4,5,8-tetra N-oxide-bis([1,2,3]triazolo)[4,5-b:5',4'-e]pyrazine (**1**), 1,7-dinitro-3,5,8-tri N-oxide-bis([1,2,3]triazolo)[4,5-b:5',4'-e]pyrazine (**2**), 1,7-dinitro-3,5-bis N-oxide-bis([1,2,3]triazolo)[4,5-b:5',4'-e]pyrazine (**3**), 1,7-dinitro-1,7-dihydrobis([1,2,3]triazolo)[4,5-b:4',5'-e]pyrazine (**4**) molecules.

Using this predicted data, we then ran Cheetah calculations to predict the performance of these materials. Additionally, we predicted the qualitative impact sensitivities of these compounds using electrostatic potential maps. This information has been transitioned back to the requesting synthetic chemist, Dr Joseph Mannion of Naval Surface Warfare Center – Indian Head.

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List of Symbols, Abbreviations, and Acronyms

ARL	US Army Research Laboratory
g/cm^3	grams per cubic centimeter
DOD	Department of Defense
DSRC	DOD Supercomputing Resource Center
ESP	electrostatic surface potential
kcal/mol	kilocalories per mole (unit of energy)
TNT	trinitrotoluene

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